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(54) Title: METHACRYLATE MOULDING COMPOSITION FOR OBTAINING DECORATIVE COLOURED SHEET MATERIAL

(57) Abstract

A process for forming an acrylic sheet material comprises preparing a mixture comprising: (i) 20–89 %wt of an acrylic polymer which is a copolymer containing 50–99 %wt of methyl methacrylate units and 1–50 wt% of a copolymerisable alkyl acrylate; (ii) 10–80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate; and (iii) 1–40 wt% of decorative particles; and melt-moulding the mixture at a temperature above 150 °C to form a solid article. The process enables thermoformable acrylic articles which have the natural appearance of granite to be produced.

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METHACRYLATE MOULDING COMPOSITION FOR OBTAINING DECORATIVE COLOURED SHEET MATERIAL

The present invention relates to moulded plastics materials containing filler particles.

Polymeric materials may be formed in several different ways. Acrylic sheet materials are particularly useful for forming into articles such as architectural cladding, bathtubs, shower enclosures, panelling etc. Filled curable moulding compositions based on acrylic polymers which comprise a polymerisable syrup of polymer in monomer, usually containing a high proportion of filler particles are widely used for moulding into kitchen sinks etc. The cured articles have superior properties imparted by the fillers in the moulding composition and the high molecular weight and crosslinking of the polymer. Although the casting process produces a very good product it is relatively expensive because each article must be made separately on a batch basis. Thick sheets of cured acrylic composite material may also be made by a continuous casting process. An example of such a sheet is "Corian" ™ sold by DuPont. These materials are useful for making articles such as work surfaces, however they are rigid and not easily shapeable and usually must be cut and glued together to form 3-dimensional shapes. Also the continuous casting process requires very specialised processing equipment since the curing of cast syrup must be done under controlled conditions to produce optimum product quality. There is therefore a need for a polymeric material which has some of the benefits of filled acrylic composite materials but which may be shaped by thermoforming techniques. There is also a need for a method of making polymeric composite articles using cheaper processing methods.

According to the invention a process for forming an acrylic material comprises preparing a mixture comprising:

(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate;

(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate;

(iii) 1 - 40 wt % of decorative particles;

and melt-moulding the mixture at a temperature above 150 °C to form a solid article.

According to a second aspect of the invention we provide a melt-mouldable composition comprising :

(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate or other methacrylate;

(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate; and

(iii) 1 - 40 wt % of decorative particles.

The acrylic material may be further shaped by thermoforming techniques into useful articles such as contoured worktops or vanity unit surfaces, especially when the material is in the form of a sheet. Also multi-layer structures may be made by laminating the acrylic composite sheet to a substrate material or by coextruding the acrylic composite onto a thermoplastic substrate or by extrusion coating onto e.g. a board substrate.

The production of filled acrylic articles by melt processing is more economical than casting and curing polymerisable compositions so the benefits of a filled acrylic material may be achieved at relatively low cost. The articles produced in this way have a solid look and feel and the natural look of stone may be achieved by selecting appropriate colours and particles.

The acrylic copolymer is a copolymer of methyl methacrylate. 50 - 99% by weight of the monomer units from which it is formed are derived from methyl methacrylate monomer. The remaining units comprise one or more copolymerisable alkyl acrylate or other methacrylate units, which may include functionalised alkyl acrylates. Preferred acrylates include C_1 - C_8 alkyl acrylate, especially methyl, ethyl and butyl acrylate. Particularly preferred copolymers are derived from 70 - 95 % methyl methacrylate and 5 - 30 % of C_1 - C_4 alkyl acrylate units. The resulting copolymer preferably has a Tg of at least 60 °C.

The acrylic copolymer may be made by any known polymerisation methods, especially solution, dispersion or bulk polymerisation. The polymer may contain residues of a polymerisation initiator, or other process additive. Preferred polymers also contain residues derived from polymerisation controllers such as chain transfer agents which are added to control molecular weight. Especially preferred additives include those chain

transfer agents which also enhance the thermal stability of the polymer such as mercaptans, e.g. alkyl mercaptans. Suitable mercaptans and polymerisation methods using mercaptans as chain transfer agents in the production of acrylic polymers are already well known in the art.

The acrylic copolymer is mouldable in its molten form, i.e. it is of a grade of acrylic polymer which is generally classed as suitable for moulding. The melt flow index (MFI) of the polymer is preferably in the range 0.5 - 25 g/10 mins at 230 °C/3.8 kg (ASTM D-1238), more preferably 0.8 - 16 g/10mins. Typically the molecular weight is between 60,000 and 180,000 preferably in the range 80,000 to 150,000 Mw, e.g. 90,000 - 120,000.

The mouldable composition comprises 20 - 89, preferably 40 - 80% wt of copolymer.

The mineral filler is a particulate mineral compound selected from alumina trihydrate (Al $(OH)_3$) (ATH), magnesium hydroxide ($Mg(OH)_2$), talc or barium sulphate. The particles preferably have an average particle size of 5 - 100 μm, e.g. about 10 - 20 μm. The mouldable composition and resulting article may contain 10 - 80 wt% of the filler, preferably 10 - 50 wt%. A mixture of more than one mineral compound may be used as the filler.

The melt-mouldable mixture and resulting moulded article also contain decorative particles, e.g. coloured particles which provide a decorative effect to the sheet. Suitable particles include polymeric particles such as coloured polyester or cross-linked acrylic particles of e.g. 5 - 5000 μm average size. The decorative particles may contain colourants, opacifiers, fillers, plasticisers, stabilisers, lubricants etc. The mixture may contains 1 - 40 % of such coloured particles, preferably 10 - 30 % wt, more preferably 5 - 20 % wt. A mixture of different coloured particles may be used to provide different appearances, e.g. to simulate the appearance of natural materials such as stone or granite.

The mixture may also contain other additives, such as stabilisers, toughening agents, lubricants, pigments and dyes. Suitable toughening agents include rubbers e.g. MBS rubber, core-shell particle toughening agents, e.g. graft copolymer core shell particles made from butyl acrylate and MMA, SEBS, Kraton, or SBR etc. The toughening agent

may be present in the polymer at levels of 1 - 50%, more typically 3 - 25% A pigment or dye may be present in the polymer prior to mixing the polymer with the filler and other ingredients.

By melt-moulding we mean forming a shaped article by moulding under conditions, especially temperature, in which the polymer is molten and can be caused to flow and then cooling below the melt temperature such that the mixture retains the shape formed when the polymer was molten. Preferred such methods include extrusion and injection moulding. Preferably the moulding temperature is less than 270 °C and is more preferably 150 - 220 °C. The moulding temperature must be maintained below the decomposition temperature of any of its constituents. For example, when ATH is used as the filler then the temperature should be maintained below the decomposition temperature of ATH.

In one preferred form we provide a process for forming an acrylic article comprising the steps of feeding to an extruder a mixture comprising:
(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate;
(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate;
(iii) 1 - 40 wt % of decorative particles;
and extruding the mixture at a temperature above 150 °C through a die and subsequently cooling the extrudate to form a solid article.

In a second preferred form we provide a process for forming an acrylic article comprising the steps of forming a mixture comprising:
(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate;
(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate;
(iii) 1 - 40 wt % of decorative particles;
and injection-moulding the mixture at a temperature above 150 °C into a mould to form a solid article.

A preferred form of article is a sheet, which may vary in thickness between <1 mm and about 20 mm, e.g. 1 - 10 mm. Many other shapes of articles are possible, especially when using injection moulding techniques to melt mould the article.

We also provide a thermoformable article, preferably in the form of a sheet, comprising
(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate;
(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate;
(iii) 1 - 40 wt % of decorative particles.

The invention will now be further described in the following examples.

Example 1

1600 g of a copolymer of methyl methacrylate (PMMA) with about 12 wt % ethyl acrylate having an average molecular weight (Mw) of around 90,000 (by GPC using PMMA standards) and MFI of 13 g/10min as measured at 230 °C/3.8 kg was mixed with 400 g (20 wt%) of fine mineral particles of alumina trihydrate (ATH) with mean particle size of 8 μm, and 300 g (13 wt %) of a 1:1 mixture of black and white decorative coloured polyester particles having an average particle size of 0.1 to 0.6 mm (supplied by the J. Marshall company). The mixture was dry blended at first and then delivered to an extruder and passed through a die at 180 °C to shape it into a 3 mm thick flat sheet. It was cooled and slightly pressed between two rotating rollers which were operating at room temperature. The resulting extruded tape had the appearance of a granite material.

Example 2

Example 1 was repeated with 1 wt% of lubricant PTFE particles added to the mixture at the dry blending operation stage. The new mixture was extruded into 3 mm sheet using an average extrusion temperature of 170 °C.

Example 3

5w% of MBS toughening agent was added to the mixture in Example 1, dry blended and extruded at 180 °C. A sheet with natural granite appearance was made. Its properties are given in Table 1.

Example 4

The base polymer used in Example 1 was pigmented by the use of known mineral based pigments frequently used in conjunction with acrylics products. Samples having the appearance of various granites from white to pink, to grey, to red were made.

Example 5

The ATH filler used in Example 1 was replaced with a more thermally stable magnesium hydroxide material (at 20 wt %) with an average particle size of about 2 - 5 microns. A 3mm thick sheet with granite appearance was made.

Example 6

Example 1 was repeated but coloured polyester decorative particles with much larger particle size in the range 1 to 1.4 mm were used.

Example 7 - preparation of thermoformed article

The sheet made in Example 1 was thermoformed into a small cup using the following conditions:

Composite polymer sheet of 3 mm thickness was cut to 14 cm x 16.5 cm to allow it to be secured onto the mould . The mould and polymer assembly were then placed in an electric oven preheated at 170 °C. After 30 minutes a two stage rotary vacuum pump was attached to the mould and maximum vacuum applied. Once thermoforming had been completed the oven heating was turned off and vacuum continued to be applied until the PMMA surface temperature had dropped to 80 °C. A cup with diameter of 60 mm and depth of 25 mm was successfully vacuum formed from this material.

Example 8

Example 1 was repeated but instead of extruding the mixture it was injection moulded into test pieces, using a conventional injection moulding machine with the barrel temperature setting of around 190 °C. The test pieces had the appearance of granite, although the decorative particles were not uniformly distributed. Some of their properties are listed in Table 1.

Example 9

Example 8 was repeated using the toughened recipe of Example 3. A test piece having a granite appearance was successfully produced.

Example 10

A mixture comprising 40% ATH, 48% of the acrylic polymer used in Example 1 and 12% of the decorative particles (smaller size) were dry blended and successfully injection moulded at 190 °C.

Example 11

A mixture comprising 30% magnesium hydroxide (average particle size about 2 - 5 microns) , 58% of the acrylic polymer used in Example 1 and 12% of the decorative particles (smaller size) were dry blended and successfully injection moulded at 190 °C. The Charpy impact strength was measured as 10.52 kJm^{-2}.

Example 12

A mixture comprising 10% magnesium hydroxide, 78% of the acrylic polymer used in Example 1 and 12% of the decorative particles (smaller size) were dry blended and successfully injection moulded at 190 °C. The Charpy impact strength was measured as 17.94 kJm^{-2}.

Table 1 shows the measured properties of the samples made in some of the Examples. Flexure testing was in accordance with ISO 178 and impact testing was in accordance with ISO 179. The properties of a composite product containing about 60 wt % ATH in PMMA made by the cell cast process are also shown for comparison.

Table 1

Sample	Flex Mod (Gpa)	Flex Strength (Mpa)	Displacement At Break (mm)
Control (cast)	8.88	67.32	1.03
Example 1	3.54	69.20	2.82
Example 3	2.08	35.00	2.49
Example 8	4.14	64.92	1.80
Example 9	3.66	61.58	2.60

Claims

1. A process for forming an acrylic sheet material comprises preparing a mixture comprising:

(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate;

(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate; and

(iii) 1 - 40 wt % of decorative particles;

and melt-moulding the mixture at a temperature above 150 °C to form a solid article.

2. A process as claimed in Claim 1, wherein said copolymer comprises 70 - 95 % methyl methacrylate and 5 - 30 % of C_1 - C_4 alkyl acrylate units.

3. A process as claimed in either claim 1 or claim 2, wherein said copolymer has a Tg of at least 60°C.

4. A process as claimed in any preceding claim, wherein the mixture contains 5 - 25 % wt of decorative coloured particles.

5. A process as claimed in any preceding claim, wherein the moulding temperature is 150 - 220 °C.

6. A process as claimed in any preceding claim, wherein said melt moulding process is carried out by extrusion through a die.

7. A process as claimed in any of claims 1 - 5, wherein said melt moulding process is carried out by injection moulding said mixture into a mould.

8. A mouldable composition comprising :

(i) 20 - 89 wt% of an acrylic polymer which is a copolymer containing 50 - 99% wt of methyl methacrylate units and 1 - 50 wt% of a copolymerisable alkyl acrylate;

(ii) 10 - 80 wt% of a mineral filler composition selected from the group comprising alumina trihydrate, magnesium hydroxide, talc and barium sulphate; and

(iii) 1 - 40 wt % of decorative particles.

9. A moulding composition as claimed in claim 8, wherein said copolymer comprises 70 - 95 % methyl methacrylate and 5 - 30 % of C_1 - C_4 alkyl acrylate units.

10. A moulding composition as claimed in either claim 8 or claim 9, wherein said copolymer has a Tg of at least 60°C.

11. A moulding composition as claimed in any of claims 8 - 10, which contains 5 - 25 % wt of decorative coloured particles.

12. A moulding composition as claimed in any of claims 8 - 11, further comprising 1 - 30% of a toughening compound.

13. A moulded article in the form of a sheet of material formed by moulding a moulding composition as claimed in any of claims 8 - 12 in its molten state and subsequently cooling, said article being further shapeable above its softening point.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/03817

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L33/12 B29C45/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 280 950 A (NAGATA YOSHIAKI ET AL) 28 July 1981 (1981-07-28) claims; examples ---	1,8-12
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 435 (C-0760), 18 September 1990 (1990-09-18) & JP 02 170847 A (KYOWA GAS CHEM IND CO LTD), 2 July 1990 (1990-07-02) abstract -----	1,8,12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
28 March 2000	28. 04. 2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schueler, D

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INTERNATIONAL SEARCH REPORT	International application No. PCT/GB 99/03817

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [X] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

The term "decorative particle" is describing a subjective impression. This definition is not fulfilling the requirements of Art. 6 PCT and Rule 6bi) PCT-regulations, requiring technical characteristics. The search was performed on "pigment-containing particles".

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/03817

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4280950 A	28-07-1981	NONE	
JP 02170847 A	02-07-1990	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)